PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of

Toshiharu SAITO et al.

Serial No.: Rule 1.53(b) Div. Appln.
of Serial No. 09/295,328

Filed: April 23, 2001

For: CAPACITOR AND ITS MANUFACTURING METHOD

Prior Group Art Unit: 2831

Prior Examiner:
Anthony Dinkins

PRELIMINARY AMENDMENT

Commissioner for Patents
Washington, D.C. 20231

Sir:

Prior to examination of the above-identified application, please enter the following changes as noted below:

IN THE SPECIFICATION:

Page 1, third full paragraph, replace with the following:

Capacitors with low impedance at high frequency include ceramic capacitors, which employ ceramics as their dielectrics, and film capacitors, which employ organic polymer film as their

dielectrics. However, to achieve large capacitance, these types of capacitors require a larger size accompanied by a proportional increase in cost.

Page 4, first full paragraph, replace with the following:

The invention disclosed in Japanese Laid-open Patent No. H9-115767 employs aqueous polyacrylic acid solution as the electrodeposition solution, which is better suitable to mass production. However, the heat resistance of the polyacrylic acid electrodeposition film thus formed is not as high as that of the polyimide film. In addition, the thickness of the film tends to become thicker than that of the polyimide film, which results in smaller initial capacitance, even if the dielectric is formed by applying the same electrodeposition voltage.

Page 5, second and third full paragraphs, replace with the following:

Even if the foil is laminated, the oxide film covering of the dielectrics is thin and prone to mechanical stress, risking damage

to the oxide film during the lamination process, causing defects. Accordingly, it is considered difficult to laminate elements by applying pressure. As the number of laminated layers increases, the defect rate due to larger leak currents tends to increase in proportion. Therefore, it may be difficult to increase the rated voltage to achieve a large capacitance by increasing the number of laminated layers.

Other causes of the above problem include poor oxide film recovery capability of solid electrolyte such as polypyrrole, compared to liquid electrolyte, and difficulties in eliminating defects on the oxide film during anodization.

Page 7, second full paragraph, replace with the following:

Fig. 2 a flowchart illustrating a method of manufacturing the capacitor in accordance with the first exemplary embodiment of the present invention.

Page 13, seventh paragraph to Page 14, paragraph continued, replace with the following:

Then, in Step 4, the element onto which the first polypyrrole layer 5 is formed is immersed in a solution in a cylindrical stainless steel vessel. This solution is made by mixing 1 part of pyrrole, 1 part of solution containing 40 weight percentage of sodium salt of butyl naphthalene sulphonic acid, and 40 parts of distilled water. An external electrode is applied to the polypyrrole layer 5 to make it act as the anode, and the cylindrical stainless steel vessel acts as the cathode. Constant current with a current density of 2.5 mA/cm^2 is applied between electrodes to execute electrolytic polymerization for 30 minutes to form a second polypyrrole layer 6.

Page 21, first full paragraph, to Page 22, paragraph continued, replace with the following:

In Step 4, the element, onto which the first polypyrrole layer 13 is formed, is immersed in a cylindrical stainless vessel containing a mixed solution of one part of pyrrole, one part of 40 weight percent aqueous solution of the sodium salt of butyl naphthalene sulphonic acid as a supporting electrolyte, and 40 parts of distilled water. An external electrode is applied to the

first polypyrrole layer 13 to function as the anode, and the stainless container functions as the cathode. A constant current at a current density of 2.5 mA/cm^2 is applied between the electrodes for 30 minutes to form the second polypyrrole layer 14.

In Steps 3 and 4 of this exemplary embodiment, polypyrrole formed by chemical oxidation polymerization and electrolytic polymerization is employed as the conductor layer 11. However, the material is not limited to polypyrrole in the present invention. It is apparent that other pai-electron conjugated conductive polymers, such as polypyrrole derivatives to which alkyl groups have been introduced, and polythiophene derivatives such as polyethylene dioxythiophene are applicable. Polypyrrole or polyethylene dioxythiophenes which have high conductivity and heat resistance is preferable.

The formation method of conductive polymer is also not limited to that described in this exemplary embodiment. A conductive polymer layer may be formed on the surface of the dielectric layer only by a chemical oxydation polymerization. Negative ions used for doping the conductive polymer, such as sulphonic acid ions, are also not limited to those used in the first exemplary embodiment.

In general, any dopant used for increasing the conductivity of the conductive high polymer is suitable for the present invention.

Page 24, second and third paragraphs, replace with the following:

Table 2 shows that capacitance in the third exemplary embodiment increases in proportion to the increase in number of capacitor elements. Although capacitor elements are laminated, tan δ remains low and the same value as that of a single capacitor element. ESR is also extremely low. For 5V, leak current is small, showing no dependence on polarity. Here, leak current traveling from the aluminum foil to dielectrics is defined as positive. Low leak current and no polarity confirm the advantage of making dielectrics from organic polymer film.

In Comparison 1, mechanical stress due to friction during lamination has damaged the aluminum oxide film dielectric layer, causing a large leak current. Average tan δ of Comparison 1 exceeded that of the third exemplary embodiment. The absolute value of leak current is also larger than in the third exemplary embodiment, and polarity was even more marked.

Page 26, paragraphs 1 through 5, replace with the following:

The third exemplary embodiment enables a large capacitance to be achieved by laminating multiple capacitor elements without risking damage to the dielectric layer. This is done by configuring the laminated capacitor as multiple capacitor elements in which the conductor layer is formed on the surface of the dielectric layer made of an organic polymer film formed on a surface-roughened etched aluminum foil.

This prevents damage to the dielectric film even when pressure is applied during lamination. Many capacitor elements may be built up in layers, and a laminated capacitor with good characteristics is achieved by using organic polymer film for the dielectric layer.

Organic polymer film has better elasticity, flexibility, and slidablity than aluminum oxide film. Accordingly, it has better resistance to mechanical stress than aluminum oxidized film. Therefore, the dielectric may not be damaged even if many elements are laminated under pressure.

Aluminum oxidized film is harder than organic polymer film, but also more fragile. Accordingly, aluminum oxide film on the surface of etched aluminum foil with a complicated surface shape

may cause leak current due to the cracking as a result of mechanical stress. This increases the defect rate when manufacturing a great number of capacitors.

By adopting an organic polymer film for the dielectric layer, as in the third exemplary embodiment, a laminated capacitor with a low defect rate, good frequency characteristics, and large capacitance can be manufactured.

Page 26, sixth paragraph, to Page 27, second paragraph, replace with the following:

Since the conductor layer is mainly constituted of the conductive high polymer layer, its conductivity is extremely high, and it has good adhesion with the organic polymer constituting the dielectric layer. This achieves lower contact resistance at the boundary face, and thus lower ESR.

Since the conductive high polymer layer is made of polypyrrole formed by the combination of chemical polymerization and electrolytic polymerization, the laminated capacitor having the conductor layer with good thermal stability and high conductivity is achieved.

Since the conductor layer is made of a conductive polymer layer and graphite layer, ESR is extremely small.

Page 27, fifth full paragraph, replace with the following:

Since organic polymer film 12 is formed by electro-deposition, it covers the roughened surface of the conductor electrode evenly, making it more resistant to mechanical stress as well as having the advantage of not possessing polarity.

Page 31, first full paragraph, replace with the following:

The conductor layer 11 comprises a first polypyrrole layer 13 and second polypyrrole layer 14 which are conductive polymers, and graphite layer 15.

Page 31, fifth paragraph, to Page 31, paragraph continued, replace with the following:

Constituents of the above solution are: 10 weight % of solid resin, 60 weight % of ion exchange water, 46 weight % of N-methyl

pyrrolidone, and 4 weight % of butyl cellosolve. Same as in the third exemplary embodiment, the solid resin comprises a mixture in which copolymer of acrylic acid, methacrylic acid, and styrene (molecular weight: about 30,000) (main agent) and benzoguanamine resin (curing agent) are mixed in a weight ratio of 7 : 3. For dispersing the above resin in the solution, an appropriate amount of triethylamine is added to neutralize 50% of the carboxylic acid in the solid, as is often used in the anion electrodeposition method, and improve dispersability and electro-deposition efficiency. The pH level of this solution was 7.8, and its conductivity was 1.6 x 10-4 Scm-1. N-methyl pyrrolidone added has a function to increase fusion of copolymers for electro-deposition, and suppress formation of a high polymer film in the electro-deposition solution.

Page 32, third full paragraph to Page 34, paragraph continued, replace with the following:

How the above phenomenon is achieved is described next. On the electrode of the etched aluminum foil 9, which is anode, deposition of a high polymer film by neutralization of carboxylic acid ion

containing high polymers and hydrogen ion generated by electrolysis of water, and oxidization of aluminum compete. In this solution, a normal electrode potential of aluminum is as low as -1.66V compared to the normal hydrogen electrode potential. Accordingly, oxidization of aluminum is likely to occur thermodynamically. N-methyl pyrrolidone which occupies as large percentage as 46 weight % in the solution has strong capacity to dissolve polymers for electro-deposition as mentioned above so that it suppresses formation of a polymer film. Therefore, in the fifth exemplary embodiment, speed of forming the polymer film is slowed down. Under these conditions, an oxide film formed by anodization propagates at the same time as the polymer film is formed.

After rinsing the etched aluminum foil 9 onto which the insulating film is formed by the above treatment, the specimen is dried at 80-C for 20 minutes, and then heat treated at 180-C for 30 minutes to cure polyacrylic acid derived resin with benzoguanamine resin.

The above electro-deposition, anodization, and heat treatment are repeated three times. Set voltage is increased in steps of 20 V, 30 V, and 40 V. This makes it possible to manufacture an element with a composite dielectric layer comprised of polyacrylic acid

derived resin film 12 and aluminum oxide film 18 with good heat resistance and insulation performance.

Only aluminum of the above composite dielectric layer is dissolved with a bromine-methanol solution to observe a cross section of the composite dielectric layer with a scanning electronic microscope (SEM). As a result, the polyacrylic acid derived rein film 12 and aluminum oxide film 18 are formed at a film thickness ratio of 1:3. The aluminum oxide film in the amorphous phase, but a dense film was formed.

Page 37, first and second paragraphs, replace with the following:

The method of manufacturing the laminated capacitor in the fifth exemplary embodiment comprises the steps of forming the compound dielectric layer consisting of the organic polymer film and the oxide film of the conductor electrode at a specified area of the surface-roughened conductor electrode; forming the insulating layer for preventing any electrical contact between the surface-roughened conductor electrode and the conductor layer; completing the capacitor element by forming the conductor layer on

the dielectric layer surface; laminating multiple capacitor elements and bonding adjacent conductor electrodes with conductive adhesive; bonding adjacent surface-roughened conductor electrodes to achieve electrical contact; and providing the terminal electrode. This enables to increase dielectric constant of the dielectric layer compared to the dielectric layer formed only of the organic polymer film, realizing the manufacture of a small laminated capacitor with large capacitance made by laminating multiple capacitor elements without damaging the dielectric layer.

In the step of forming the compound dielectric layer consisting of the organic polymer film and the oxide film of the conductor, both electro-deposition method and anodization method are employed. This enables to form the compound dielectric layer with good insulation performance by covering the surface-roughened conductor layer uniformly.

<u>IN THE CLAIMS</u>:

Please cancel claims 1-36.

Please amend claims 41-43 as follows:

41. (Amended) A method of manufacturing laminated capacitors, said method comprising the steps of:

forming one of:

dielectrics made of organic polymer, and composite dielectrics made of organic polymer and oxide of a metal constituting said conductor;

forming an insulating layer at least on said conductor;

forming an opposite electrode on said dielectrics to complete a capacitor element;

laminating a plurality of said capacitor elements; and

forming an external connection terminal.

42. (Amended) The method of manufacturing the laminated capacitors as defined in Claim 41, wherein said dielectrics is formed by electro-depositing organic polymer.

43. (Amended) The method of manufacturing laminated capacitors as defined in Claim 41, wherein said compound dielectrics is formed by simultaneous progression of:

electrodeposition of organic polymer; and

anodization of a metal constituting said conductor.

REMARKS

This application is a Rule 1.53(b) Divisional Application of Serial No. 09/295,328, filed April 21, 1999, now allowed.

Claims 37-46 remain pending herein. Claims 41, 42, and 43 have been amended hereby. Claims 1-36 have been cancelled without prejudice or disclaimer.

The specification and claims have been amended in the same manner as in the parent application and to identify the parent application.

Filed herewith is an Information Disclosure Statement listing all references cited during prosecution of the parent application.

Prompt and favorable examination of this application on the merits is respectfully solicited.

Respectfully submitted,

PARKHURST & WENDEL, L.L.P.

Date: April 23, 2001

Roger W. Parkhurst
Registration No. 25,177

Attachment:
Mark Up of Specification and Claims

RWP/ame

Attorney Docket No. MEIC:047A

PARKHURST & WENDEL, L.L.P.
1421 Prince Street, Suite 210
Alexandria, Virginia 22314-2805
Telephone: (703) 739-0220

CAPACITOR AND ITS MANUFACTURING METHOD

FIELD OF THE INVENTION

The present invention relates to the field of capacitors employed in electronic circuits for electric equipment, electronic equipment, and acoustic equipment.

BACKGROUND OF THE INVENTION

The demand for smaller electronic components with higher performance and reliability is continuing to grow as equipment becomes smaller, thinner, and lighter, and electrical equipment circuits become more densely packed and digitized. There is, as a result, an accelerating demand for capacitors with the characteristics of smaller size, larger capacitance, and lower impedance at high frequencies.

Capacitors with low impedance at high frequency include ceramic capacitors, which employ ceramics as their dielectrics, and film capacitors, which employ organic ~~high~~ polymer film as their dielectrics. However, to achieve large capacitance, these types of capacitors require a larger size accompanied by a proportional increase in cost.

On the other hand, electrolytic capacitors, which employ aluminum or tantalum oxide film as their dielectrics, can achieve large capacitance with small size; however, their impedance and dielectric characteristics in the high frequency band degrade comparing with those of the aforementioned ceramic capacitors and film capacitors. Therefore, to improve their high frequency characteristics, aluminum solid electrolytic

electrodeposition requires to be heat treated at above 200 °C to imidize the film.

Polyamic acid, when exposed to a high-humidity atmosphere, easily decomposes and shows low stability in storage. Accordingly, the molecular weight may deviate even when polyamic acid film is electrodeposited and then imidized by heat treatment. The durability of the film is also poor. Since the film quality is not ideal, capacitors using polyimide film created by heat treating polyamic acid electrodeposited film show deviations in dielectric characteristics. In addition, the capacitance of polyimide film drops considerably over time if voltage is continuously applied at temperatures between 80 and 200 °C.

The invention disclosed in Japanese Laid-open Patent No. H9-115767 employs aqueous polyacrylic acid solution as the electrodeposition solution, which is better suitable to mass production. However, the heat resistance of the polyacrylic acid electrodeposition film thus formed is not as high as that of the polyimide film. In addition the thickness, the film tends to become thicker than that of the polyimide film, which results in smaller initial capacitance, even if the dielectric is formed by applying the same electrodeposition voltage.

The present invention solves the above problems with conventional techniques and aims to provide a small capacitor with high productivity, non-polar characteristics, and large capacitance, and its manufacturing method by adopting a new polyimide as a dielectric material.

Next, the second concern which the present invention aims to solve is described.

In response to the demand for smaller electronic equipment and to the demand for high frequency switching power supply, attempts are being made to increase the capacitance of aluminum solid electrolytic capacitors using TCNQ complex or polypyrrole for the cathode by rolling or laminating etched aluminum foil.

If etched aluminum foil is rolled, mechanical stress is applied to the bent portions, which may damage the oxide film and degrade its electrical characteristics.

Even if the foil is laminated, the oxide film ~~covering~~ of the dielectrics is thin and prone to mechanical stress, risking damage to the oxide film during the lamination process, causing defects. Accordingly, it is considered difficult to laminate elements by applying pressure. As the number of laminated layers increases, the defect rate due to larger leak currents tends to increase in proportion. Therefore, it may be difficult to increase the rated voltage to achieve a large capacitance by increasing the number of laminated layers.

Other causes of the above problem include poor oxide film recovery capability of solid electrolyte such as polypyrrole, compared to liquid electrolyte, and difficulties in eliminating defects on the oxide film during anodization.

Accordingly, it may be difficult to increase capacitance by simultaneously increasing the number of laminated layers and the rated voltage for solid electrolytic capacitors that employ an oxide film dielectrics.

using a solution or dispersed solution containing polyimide as the electrodeposition solution; drying the polyimide film and heat treating it; and forming an opposite electrode on the polyimide film.

Another method for manufacturing the capacitor of the present invention comprises the steps of forming dielectrics made of an organic high polymer film or compoosite dielectrics made of organic high polymers and metal oxide on the surface of a conductor with roughened surface; forming an insulating layer on the conductor; constructing a capacitor element by forming an opposite electrode on the dielectrics; laminating more than one above capacitor elements; and forming an external connection terminal.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 a schematic sectional view of a capacitor in accordance with a first exemplary embodiment of the present invention.

Fig. 2 a ~~flow~~ flowchart illustrating a method of manufacturing the capacitor in accordance with the first exemplary embodiment of the present invention.

Fig. 3 a schematic sectional view of a capacitor in accordance with a second exemplary embodiment of the present invention.

Fig. 4 a flowchart illustrating a method of manufacturing the capacitor in accordance with the second exemplary embodiment of the present invention.

A constant 40 V is applied between both electrodes for 1 minute to form the dielectric polyimide film 2 onto the surface of the etched aluminum foil electrode 4.

It is apparent that the thickness of the polyimide film 2 is adjustable by changing the applied voltage, the duration of electrodeposition, and the number of electrodepositions.

In Step 2, the specimen onto which the dielectric layer is formed is rinsed, dried at 80 °C for 20 minutes, and then heat treated at 180 °C for 30 minutes to evaporate the solvent in the polyimide film 2 to complete the polyimide film 2.

In Step 3, the element is immersed alternately for 2 minutes each in ethanol solution containing 1.0 mol/l pyrrole and 1.0 mol/l ammonium persulfate aqueous solution three times to form the first polypyrrole layer 5 made of chemically oxypolymerized polypyrrole film.

Then, in Step 4, the element onto which the first polypyrrole layer 5 is formed is immersed in a solution in a cylindrical stainless steel vessel. This solution is made by mixing 1 part of pyrrole, 1 part of solution containing 40 weight percentage of sodium salt of butyl naphthalene sulphonic acid, and 40 parts of distilled water. An external electrode is applied to the polypyrrole layer 5 to make it act as the anode, and the cylindrical stainless steel vessel acts as the cathode. Constant current with a current density of 2.5 mA/cm~~2~~^{2} is applied between electrodes to execute ~~electro~~ electrolytic polymerization for 30 minutes to form a second polypyrrole layer 6.

of ammonium persulfate alternately for two minutes each for three times to form the first polypyrrole layer 13 on the dielectric layer.

In Step 4, the element, onto which the first polypyrrole layer 13 is formed, is immersed in a cylindrical stainless vessel containing a mixed solution of one part of pyrrole, one part of 40 weight percent aqueous solution of the sodium salt of butyl naphthalene sulphonic acid as a supporting electrolyte, and 40 parts of distilled water. An external electrode is applied to the first polypyrrole layer 13 to function as the anode, and the stainless container functions as the cathode. A constant current at a current density of 2.5 mA/cm~~2~~^{2} is applied between the electrodes for 30 minutes to form the second polypyrrole layer 14.

In Steps 3 and 4 of this exemplary embodiment, polypyrrole formed by chemical oxidation polymerization and ~~electro-~~ electrolytic polymerization is employed as the conductor layer 11. However, the material is not limited to polypyrrole in the present invention. It is apparent that other ~~π~~ pai-electron conjugated conductive polymers, such as polypyrrole derivatives to which alkyl groups have been introduced, and polythiophene derivatives such as polyethylene dioxythiophene are applicable. Polypyrrole or polyethylene dioxythiophenes which have high conductivity and heat resistance is preferable.

The formation method of conductive ~~high-~~polymer is also not limited to that described in this exemplary embodiment. A conductive ~~high~~ polymer layer may be formed on the surface of the dielectric layer only by a chemical oxydation polymerization. Negative ions used for doping the conductive polymer, such as sulphonic acid ions, are also not limited to

treatment process. The heat treatment temperature for the anodized film was set to be 480 °C. The apparent area of one side of the etched aluminum foil onto which the dielectrics is formed was 3 mm x 4 mm. Except for the process to form dielectrics by anodization, the same procedures from Steps 2 to 8 as in the third exemplary embodiment were implemented to laminate five capacitor elements each, to manufacture five laminated capacitors in total. Comparison 1 shows the capacitance at 120 Hz, tan δ at 120 Hz, ESR at 100 kHz, and average leak current when applying plus minus 5V.

Table 2 shows that capacitance in the third exemplary embodiment increases in proportion to the increase in number of capacitor elements. Although capacitor elements are laminated, tan δ remains low and the same value as that of a single capacitor element. ESR is also extremely low. For 5V, leak current is small, showing no dependence on polarity. Here, leak current traveling from the aluminum foil to dielectrics is defined as positive. Low leak current and no polarity confirm the advantage of making dielectrics from organic ~~high-~~polymer film.

In Comparison 1, mechanical stress due to friction during lamination has damaged the aluminum oxide film dielectric layer, causing a large leak current. Average tan δ of ~~Comparison 1exceeded~~ Comparison 1 exceeded that of the third exemplary embodiment. The absolute value of leak current is also larger than in the third exemplary embodiment, and polarity was even more marked.

When comparing the ESR of the third exemplary embodiment and that of Comparison 1, the laminated capacitor in the third exemplary

capacitor in the third exemplary embodiment is smaller but has a larger capacitance than conventional film capacitors. This was made possible by employing roughened electrodes in the capacitor elements and laminated multiple capacitor elements.

The third exemplary embodiment enables a large capacitance to be achieved by laminating multiple capacitor elements without risking damage to the dielectric layer. This is done by configuring the laminated capacitor as multiple capacitor elements in which the conductor layer is formed on the surface of the dielectric layer made of an organic ~~high~~ polymer film formed on a surface-roughened etched aluminum foil.

This prevents damage to the dielectric film even when pressure is applied during lamination. Many capacitor elements may be built up in layers, and a laminated capacitor with good characteristics is achieved by using organic ~~high-~~polymer film for the dielectric layer.

Organic ~~high-~~polymer film has better elasticity, flexibility, and slidablity than aluminum oxide film. Accordingly, it has better resistance to mechanical stress than aluminum oxidized film. Therefore, the dielectric may not be damaged even if many elements are laminated under pressure.

Aluminum oxidized film is harder than organic ~~high-~~polymer film, but also more fragile. Accordingly, aluminum oxide film on the surface of etched aluminum foil with a complicated surface shape may cause leak current due to the ~~of~~ cracking as a result of mechanical stress. This increases the defect rate when manufacturing a great number of capacitors.

By adopting an organic ~~high~~ polymer film for the dielectric layer, as in the third exemplary embodiment, a laminated capacitor with a low defect rate, good frequency characteristics, and large capacitance can be manufactured.

Since the conductor layer is mainly constituted of the conductive high polymer layer, its conductivity is extremely high, and it has good adhesion with the organic ~~high~~ polymer constituting the dielectric layer. This achieves lower contact resistance at the boundary face, and thus lower ESR.

Since the conductive high polymer layer is made of polypyrrole formed by the combination of chemical polymerization and ~~electro-~~ electrolytic polymerization, the laminated capacitor having the conductor layer with good thermal stability and high conductivity is achieved.

Since the conductor layer is made of a conductive ~~high~~ polymer layer and graphite layer, ESR is extremely small.

In the capacitor of this exemplary embodiment, multiple capacitor elements are laminated in the same directions, and conductor layers of adjacent capacitor elements are adhered to by conductive adhesive, and bonded so that electrodes with roughened surface area are also electrically conductive. Multiple capacitor elements are electrically connected in parallel. This achieves a laminated capacitor with large capacitance.

By providing an insulating layer for preventing electrical contact of the conductor with roughened surface and the conductor layer formed on the surface of the dielectric layer, multiple capacitor elements can be

easily connected in parallel without the risk of electrical contact between capacitor elements.

Since organic ~~high~~ polymer film ~~2~~ 12 is formed by electro-deposition, it covers the roughened surface of the conductor electrode evenly, making it more resistant to mechanical stress as well as having the advantage of not possessing polarity.

Since the dielectric film used in the capacitor is a polyacrylic acid resin film formed by electro-deposition, it shows good adhesion with etched aluminum foil, strong mechanical stress, and good insulation characteristics.

The method of manufacturing the laminated capacitor in the third exemplary embodiment comprises the steps of forming an organic high polymer dielectric layer onto a specified portion of the roughened surface of the conductor electrode; forming an insulating layer to prevent electrical contact between the conductor electrode and the conductor layer; completing the capacitor laminated by forming the conductor layer on the surface of the dielectric layer; laminating multiple capacitor elements and adhering adjacent conductor layers by conductive adhesive; bonding adjacent conductor electrodes with roughened surface area to ensure electrical contact; and providing terminal electrodes. This allows the lamination of multiple capacitor elements without damaging the dielectric layer, resulting in feasible manufacture of a small laminated capacitor with good characteristics and large capacitance.

Since the electro-deposition method is employed in the step of forming the dielectric layer of organic high polymer film, the conductor

In Fig. 12, a compound dielectric layer, a dielectric layer of organic high polymer film, comprising a polyacrylic acid derived resin film 12 and an aluminum oxide film 18, is formed by means of electro-deposition and anodization which covers the surface following the surface shape of an etched aluminum foil 9. A conductor layer 11 is further formed on the surface of the composite dielectric layer. Then, an insulating layer 10 is provided on the surface of the composite dielectric layer to prevent any electrical contact between the etched aluminum foil 9 and conductor layer 11.

The conductor layer 11 comprises a first polypyrrole layer 13 and second polypyrrole layer 14 which are conductive ~~high~~ polymers, and graphite layer 15.

The capacitor element in the fifth exemplary embodiment as described above only differs with that of the third exemplary embodiment by the structure for the dielectric layer. In other words, when multiple capacitor elements in the fifth exemplary embodiment are laminated, the laminated capacitor having the structure shown in Fig. 7 is also achieved.

Next, an example of a method for manufacturing the laminated capacitor with the above structure is described in details with reference to a flow chart in Fig. 13.

First, solutions to be used for electro-deposition and anodization are described first. In the solution, the main agent of polyacrylic acid derived resin and curing agent of benzoguanamine resin are dispersed in the form of a micelle structure. When the micelle diameter was measured

using the dynamic scattering method, its average diameter was shown to be about 0.05 μm.

Constituents of the above solution are: 10 weight % of solid resin, 60 weight % of ion exchange water, 46 weight % of N-methyl pyrrolidone, and 4 weight % of butyl cellosolve. Same as in the third exemplary embodiment, the solid resin comprises a mixture in which copolymer of acrylic acid, methacrylic acid, and styrene (molecular weight: about 30,000) (main agent) and benzoguanamine resin (curing agent) are mixed in a weight ratio of 7 : 3. For dispersing the above resin in the solution, an appropriate amount of ~~triethyl amine~~ triethylamine is added to neutralize 50% of the carboxylic acid in the solid, as is often used in the anion electrodeposition method, and improve dispersability and electro-deposition efficiency. The pH level of this solution was 7.8, and its conductivity was 1.6 x 10-4 Scm-1. N-methyl pyrrolidone added has a function to increase fusion of copolymers for electro-deposition, and suppress formation of a high polymer film in the electro-deposition solution.

Next, Step 1 is described. First, the above solution is poured into a cylindrical stainless steel vessel, which acts as the cathode, with a diameter of 80 mm,. Then, the etched aluminum foil 9 cut into a piece 9 mm x 5 mm in size is immersed in the solution to act as the anode. The area immersed is 5 x 5 mm. The etched aluminum foil 9 used in this step is previously electro-cleaned using alkali solution to remove the natural oxide film on the surface and make the surface uniform. Before applying voltage, any air remaining in the fine pores of the etched aluminum foil 9

is degassed under reduced pressure to ensure that all the fine pores are completely filled with solution.

Next, the current is applied according to the constant current method at a current density of 0.2 mA/cm^2. After reaching a target voltage of 10V, voltage is continued to be applied at the constant voltage until total time of applying current and voltage reaches 30 minutes. This enables to form the polyacrylic acid derived resin film 12 and aluminum oxide film 18 simultaneously on the surface of the etched aluminum foil 9.

How the above phenomenon is achieved is described next. On the electrode of the etched aluminum foil 9, which is anode, deposition of a high polymer film by neutralization of carboxylic acid ion containing high polymers and hydrogen ion generated by electrolysis of water, and oxidization of aluminum compete. In this solution, a normal electrode potential of aluminum is as low as -1.66V compared to the normal hydrogen electrode potential. Accordingly, oxidization of aluminum is likely to occur thermodynamically. N-methyl pyrrolidone which occupies as large percentage as 46 weight % in the solution has strong capacity to dissolve ~~high-~~polymers for electro-deposition as mentioned above so that it suppresses formation of a ~~high-~~polymer film. Therefore, in the fifth exemplary embodiment, speed of forming the ~~high-~~polymer film is slowed down. Under these conditions, an oxide film formed by anodization propagates at the same time as the ~~high-~~polymer film is formed.

After rinsing the etched aluminum foil 9 onto which the insulating film is formed by the above treatment, the specimen is dried at 80°C for 20

minutes, and then heat treated at 180°C for 30 minutes to cure polyacrylic acid derived resin with benzoguanamine resin.

The above electro-deposition, anodization, and heat treatment are repeated three times. Set voltage is increased in steps of 20 V, 30 V, and 40 V. This makes it possible to manufacture an element with a composite dielectric layer comprised of polyacrylic acid derived resin film 12 and aluminum oxide film 18 with good heat resistance and insulation performance.

Only aluminum of the above composite dielectric layer is dissolved with a ~~boron~~bromine-methanol solution to observe a cross section of the composite dielectric layer with a scanning electronic microscope (SEM). As a result, the polyacrylic acid derived rein film 12 and aluminum oxide film 18 are formed at a film thickness ratio of 1:3. The aluminum oxide film in the amorphous phase, but a dense film was formed.

In Step 1, the thickness of the polyacrylic acid derived resin film 12 and aluminum oxide film 18 is adjustable by changing the solution mixing ratio, current density, set voltage, and duration of electro-deposition.

A method for forming the composite dielectric layer of the present invention is not limited to the method described in the fifth exemplary embodiment. An organic high polymer film may be electro-deposited onto an aluminum foil which is previously anodized. Solution containing organic acid salt or inorganic salt effective for anodizing, such as ammonium adipate, mixed with high polymers for electro-deposition as described in the third exemplary embodiment may be used for electro-deposition and anodization.

becomes low and ESR remains low, same as in the third exemplary embodiment.

Since the conductive high polymer layer is formed by polypyrrole using both chemical oxidation polymerization and electro-polymerization, a laminated capacitor having the conductor layer with high conductivity and good heat stability is achievable.

Since the conductor layer is formed of the conductive high polymer layer and graphite layer, ESR became extremely small.

Multiple capacitor elements are aligned in the same directions for lamination, and the conductor layers acting as opposite electrodes to adjacent capacitor elements are bonded by the conductive adhesive, and then conductor electrodes themselves are bonded to achieve electrical contact so that multiple capacitor elements are electrically connected in parallel. This enables to achieve the laminated capacitor with large capacitance.

The insulating layer is provided to prevent any electrical contact between the surface-roughened conductor and the conductor layer formed on the dielectric layer. This facilitates parallel connection of multiple capacitor elements without electrical contact between capacitor elements.

The method of manufacturing the laminated capacitor in the fifth exemplary embodiment comprises the steps of forming the compound dielectric layer consisting of the organic ~~high~~ polymer film and the oxide film of the conductor electrode at a specified area of the surface-roughened conductor electrode; forming the insulating layer for preventing any electrical contact between the surface-roughened conductor electrode and

the conductor layer; completing the capacitor element by forming the conductor layer on the dielectric layer surface; laminating multiple capacitor elements and bonding adjacent conductor electrodes with conductive adhesive; bonding adjacent surface-roughened conductor electrodes to achieve electrical contact; and providing the terminal electrode. This enables to increase dielectric constant of the dielectric layer compared to the dielectric layer formed only of the organic ~~high~~ polymer film, realizing the manufacture of a small laminated capacitor with large capacitance made by laminating multiple capacitor elements without damaging the dielectric layer.

In the step of forming the compound dielectric layer consisting of the organic ~~high-~~polymer film and~~ conductor oxide film~~ the oxide film of the conductor, both electro-deposition method and anodization method are employed. This enables to form the compound dielectric layer with good insulation performance by covering the surface-roughened conductor layer uniformly.

The organic high polymer film used in forming the above dielectric layer is a polyacrylic acid derived resin film which is a typical polycarboxylic acid resin. This allows to efficiently solidify by the electro-deposition method. Thus, the non-polar dielectric layer with good heat resistance, insulation performance, and resistance to mechanical stress is achieved.

In the step of forming the conductor layer on the dielectric layer surface to complete the capacitor element, both chemical oxidation polymerization and electro-polymerization are employed for forming the

tetracarboxylic acid di-anhydride and aromatic diamine having at least one carboxylic acid radical.

39. The method of manufacturing capacitors as defined in Claim 37, wherein water is contained in said electro-deposition solution.

40. The method of manufacturing capacitors as defined in Claim 37, wherein said conductor is one of surface-roughened or perforated metal.

41. A method of manufacturing laminated capacitors, said method comprising the steps of:

forming one of:

~~dielectrics made of organic high polymer,~~ dielectrics made of organic ~~high-~~polymer and composite dielectrics made of organic ~~high~~ polymer and oxide of a metal constituting said conductor;

forming an insulating layer at least on said conductor;

forming an opposite electrode on said dielectrics to complete a capacitor element;

laminating a plurality of said capacitor elements; and

forming an external connection terminal.

42. The method of manufacturing the laminated capacitors as defined in Claim 41, wherein said dielectrics is formed by electro-depositing organic ~~high-~~polymer.

43. The method of manufacturing laminated capacitors as defined in Claim 41, wherein said compound dielectrics is formed by simultaneous progression of:

electrodeposition of organic ~~high~~ polymer; and

anodization of a metal constituting said conductor.

44. The method of manufacturing laminated capacitors as defined in Claim 41, wherein said opposite electrode is formed using one of:

chemical oxy-polymerization; and

both chemical oxy-polymerization and electro-polymerization.

45. The method of manufacturing laminated capacitors as defined in Claim 41, wherein said opposite electrodes of said adjacent capacitor elements are bonded using conductive adhesive in said step of laminating a plurality of said capacitor elements.

46. The method of manufacturing laminated capacitors as defined in Claim 41, wherein pressure is applied during bonding using said conductive adhesive.

FIG. 4

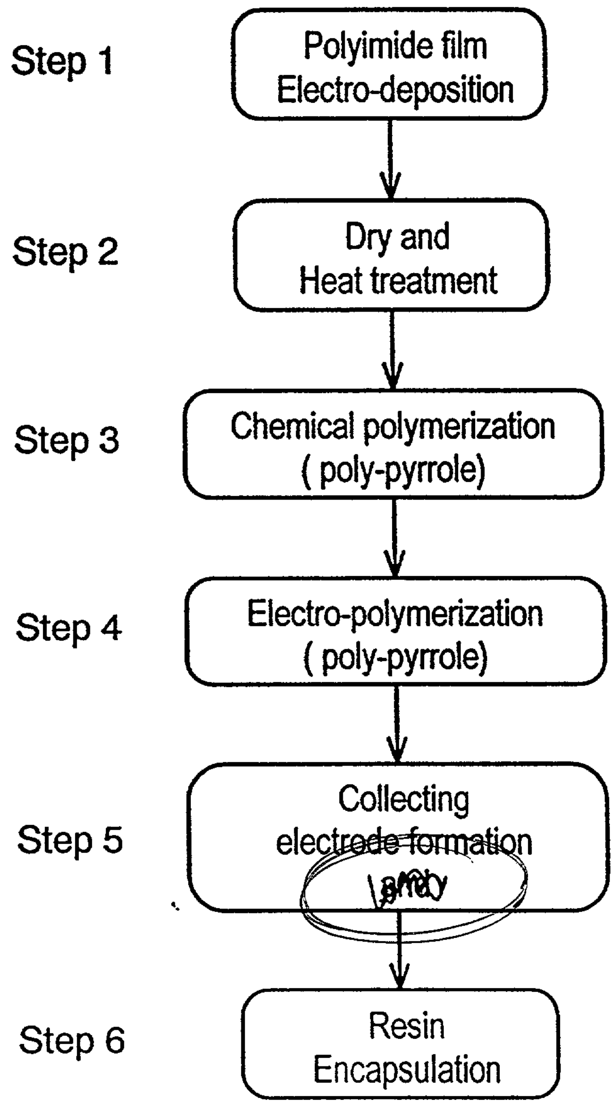
Step 1
Polyimide film Electro-deposition
Step 2
Dry and Heat treatment
Step 3
Chemical polymerization (poly-pyrrole)
Step 4
Electro-polymerization (poly-pyrrole)
Step 5
Collecting electrode formation
Step 6
Resin Encapsulation

FIG. 8

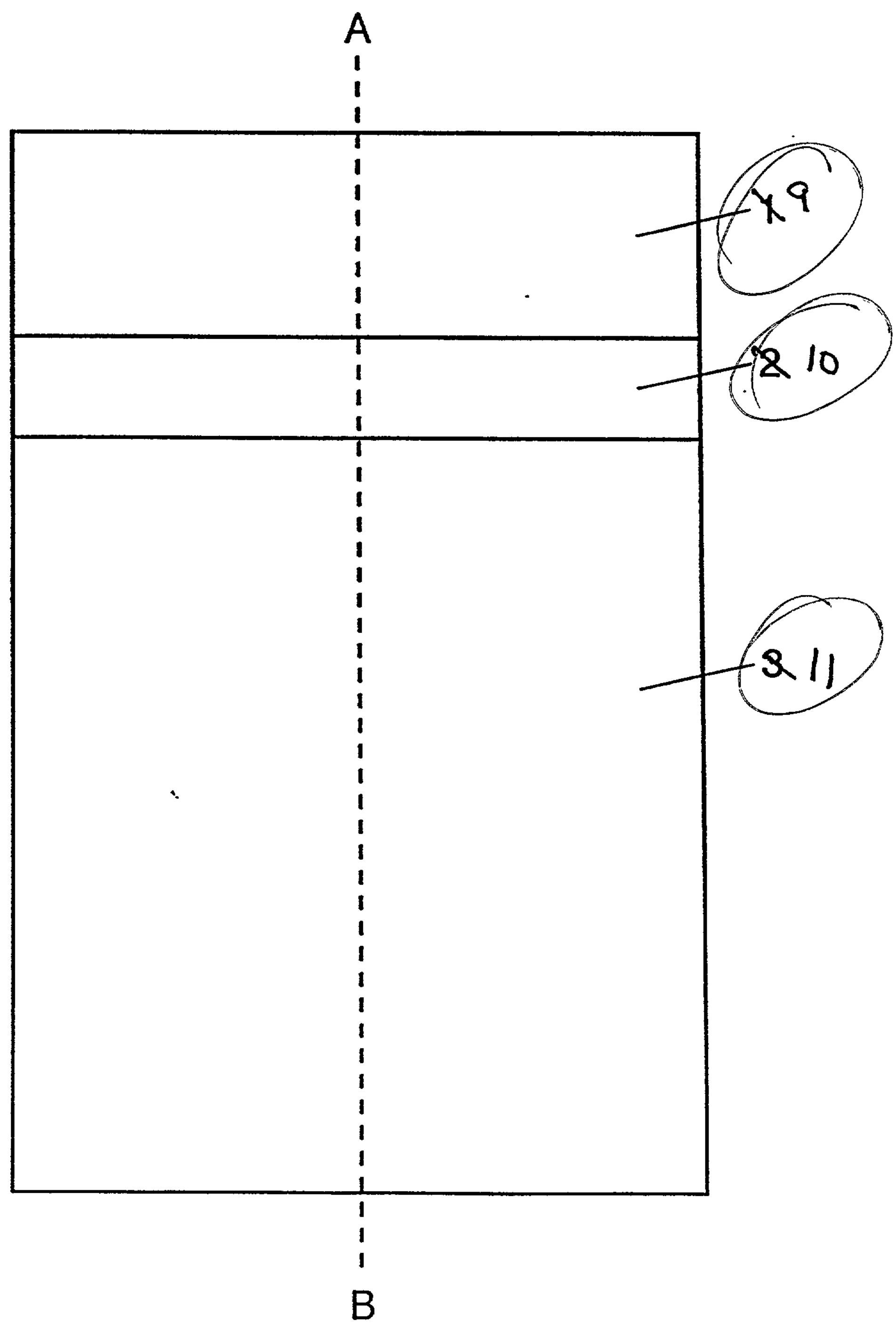

FIG. 9